



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C11D 3/386 // 3/39	A1	(11) International Publication Number: WO 00/42145 (43) International Publication Date: 20 July 2000 (20.07.00)
(21) International Application Number: PCT/US99/00790 (22) International Filing Date: 14 January 1999 (14.01.99) (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SHOWELL, Michael, Stanford [US/US]; 685 Compton Road, Cincinnati, OH 45231 (US). ZHU, Yong [CN/US]; 4348 Bromyard Avenue, Cincinnati, OH 45241 (US). MOESE, Rosa, Laura [US/US]; 8815 Eagle Creek Court, West Chester, OH 45069 (US). BETTIOL, Jean-Luc, Philippe [FR/BE]; 93 Avenue Slegers, B-1200 Brussels (BE). BUSCH, Alfred [DE/BE]; Handelsstraat 210, B-1840 Londerzeel (BE). WELLS, Eric [US/US]; 1440 W. Kemper Road #1601, Cincinnati, OH 45240 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: DETERGENT COMPOSITIONS COMPRISING A PECTIN DEGRADING ENZYMES SYSTEM (57) Abstract <p>The present invention relates to detergent compositions comprising a pectate lyase and a pectin lyase, providing superior cleaning performance, i.e. superior stain removal on plant-based stains/soils and body soils, dingy cleaning and whiteness maintenance.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

DETERGENT COMPOSITIONS COMPRISING A PECTIN DEGRADING ENZYMES SYSTEM

Field of the Invention

The present invention relates to detergent compositions comprising an enzymatic system comprising a pectate lyase (EC 4.2.2.2) and a pectin lyase (EC 4.2.2.10).

Background of the invention

Performance of a detergent product is judged by a number of factors, including the ability to remove soils, and the ability to prevent the redeposition of the soils, or the breakdown products of the soils on the articles in the wash. Therefore, detergent compositions include nowadays a complex combination of active ingredients which fulfil certain specific needs. In particular, current detergent formulations generally include surfactants and detergent enzymes providing cleaning and fabric care benefits.

Removal of stains stemming from plants, wood, mould-clay based soil, muddy soils, and fruits is one of today's toughest cleaning tasks; especially with the trend toward low wash temperatures. These stains typically contain complex mixtures of fibrous material based mainly on carbohydrates and their derivatives : fibres and cell wall components. Plant based soils are additionally accompanied with amylose, sugars and their derivatives. Food soils are often difficult to remove effectively from a soiled substrate. Highly coloured or "dried-on" soils derived from fruit and/or vegetable juices are particularly challenging to remove. Specific examples of such soils would include orange juice, tomato juice, banana, mango or broccoli soils. Indeed, pectin polymers are important constituents of plant cell walls. Pectin is a hetero-polysaccharide with a backbone composed of alternating homogalacturonan (smooth regions) and rhamnogalacturonan (hairy regions). The smooth regions are linear polymers of 1,4-linked alpha-D-galacturonic acid. The galacturonic acid residues can be methyl-esterified on the carboxyl group to a varying degree, usually in a non-random fashion with blocks of polygalacturonic acid being completely methyl-esterified. The substrates on which pectin containing stains are commonly found can be fabrics, dishware or hard surfaces.

In addition, the complex nature of everyday "body" soils typically found on pillow cases, T-shirts, collars and socks, provides a continuous thorough cleaning challenge for detergents. These soils are difficult to remove completely due in part to their interaction with the pectin components in the primary cell walls of cotton fibers comprising cotton containing fabrics, and often residues build up on such fabric leading to dinginess and yellowing. Moreover, body fluid stains, such as blood and menstrual fluids, are often difficult to remove effectively from a soiled item, especially when the stains have been aged. Everyday body soils are also found on sanitary and kitchen surfaces such as bathtubs, toilet bowls and dishware.

The use of enzymes in detergents is well-known in the art. For example, amylase enzymes have long been recognised in detergent compositions to provide the removal of starchy food residues or starchy films from dishware or hard surfaces or to provide cleaning performance on starchy soils as well as other soils typically encountered in laundry applications. Protease enzymes have long been recognised in detergent compositions to provide the removal of proteinaceous food residues from dishware, hard surfaces or to provide cleaning performance on proteinaceous soils as well as other soils typically encountered in laundry applications. Additionally, the use of cellulase is also well-known in the art. This activity in particular on fabrics provides a cleaning, rejuvenation, softening and generally improved handfeel characteristics to the fabric structure. The inclusion of lipolytic enzyme (e.g. lipase) in detergent compositions for improved cleaning performance is known, e.g. enhancement of removal of triglycerides containing soils and stains from fabrics.

Pectin degrading enzymes are known to provide soil/stain removal benefits when used in washing and cleaning operations, specifically to provide the removal of a broad range of plant and fruit based stains and enhance the body soil cleaning profile of the detergent compositions. By pectin degrading enzyme it is meant herein any enzyme which acts to break down pectin substances and pectin related substances. Pectin degrading enzymes can be classified according to their preferential substrate, highly methyl-esterified pectin or low methyl-esterified pectin and polygalacturonic acid (pectate), and their reaction mechanism, beta-elimination or hydrolysis. Pectin degrading enzymes can be mainly endo-acting, cutting the polymer at random sites within the chain to give a mixture of oligomers, or they may be exo-acting, attacking from one end of the polymer and producing monomers or dimers. Several pectinase activities acting on the smooth regions of pectin are included in the classification of enzymes provided by the Enzyme Nomenclature (1992) such as pectate lyase (EC 4.2.2.2), pectin lyase (EC 4.2.2.10), polygalacturonase (EC 3.2.1.15), exo-polygalacturonase

(EC 3.2.1.67), exo-polygalacturonate lyase (EC 4.2.2.9) and exo-poly-alpha-galacturonosidase (EC 3.2.1.82). The pectin degrading enzymes are natural mixtures of the above mentioned enzymatic activities.

Each type of pectin degrading enzyme has a unique profile of substrate specificity, activity and stability under different hardness, pH, temperature, surfactant and other detergent ingredient matrix conditions. Pectin degrading enzymes are specifically directed to degrade pectin substances and in particular plant cell walls. In particular, pectate lyase enzymes are specifically directed to pectic acid chains of plant cell walls such as low methoxy pectins (LMPs) while pectin lyase is more specifically directed towards esterified pectin chains such as high methoxyl pectins (HMPs). Moreover, it has been found that pectate lyases are metal and especially calcium sensitive, whereas pectin lyases do not require metals for stabilisation and optimum enzymatic activity.

It has been surprisingly found that a wide range of range of substrate specificity and a high flexibility toward a variety of wash conditions can be achieved with the combination of a pectate lyase and a pectin lyase. This results in synergistic cleaning and especially plant-based soil / stains and body soil removal.

It has been further found that the performance of the detergent compositions of the present invention is enhanced by the addition of a bleaching agent.

The use of pectin degrading enzymes in detergent has already been recognised in the art. The use of pectin enzyme is also recognised for the cleaning of contact lenses (US 4,710,313 - J60196724). Enzymes having a pectinase activity are described in DE 36 35 427 to increase the capacity of the detergent for removing inorganic dirt, e.g. sludges, from laundry without damaging the fibres and without discoloration to allow the use of zeolites and polycarbonate builders which have a lower capacity for dispersing inorganic materials than the phosphates. Benefits

for the use of pectin enzymes in detergent formulations, particularly those designed for use in laundry, dishwashing and household cleaning operations have been recognised in WO95/25790. JP 60226599 describes detergent compositions comprising conventional detergent actives and a cellulase and hydrolase such as hemicellulase, pectinase, amylase or protease. The combination of cellulase and hydrolase is said to give a good washing effect on inorganic fouling together with enzymatic activity. WO95/09909 describes an enzyme preparation comprising modified enzymes selected from the group of amylase, lipase, oxidoreductase, pectinase or hemicellulase; the modified enzyme having an improved performance due to an alkaline pI and/or increased surface activity obtained by chemical modification or amino acid substitution. Modified pectin and/or pectolytic and/or hemi-cellulolytic and /or lipolytic enzymes are applied advantageously in the papermaking industry and modified amylase and/or lipase in laundry and dishwashing.

In particular, Pectate lyases have been cloned from different bacterial genera such as *Erwinia*, *Pseudomonas*, *Klebsiella*, *Streptomyces*, *Penicillium*, *Bacteroides*, *Thermomonospora*, *Fusarium*, *Aspergillus* and *Xanthomonas*. Also from *Bacillus subtilis* (Nasser et al. (1993) FEBS **335**:319-326) and *Bacillus* sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. **58**:947-949) cloning of a pectate lyase has been described. Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by *Bacillus pumilus* (Dave and Vaughn (1971) J. Bacteriol. **108**:166-174), *B. polymyxa* (Nagel and Vaughn (1961) Arch. Biochem. Biophys. **93**:344-352), *B. stearothermophilus* (Karbassi and Vaughn (1980) Can. J. Microbiol. **26**:377-384), *Bacillus* sp. (Hasegawa and Nagel (1966) J. Food Sci. **31**:838-845) and *Bacillus* sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. **24**:1164-1172) has been reported. WO 98/45393 discloses detergent compositions containing protopectinase with remarkable detergency against muddy soiling.

Pectic enzymes are commonly used in the fruit/vegetable juice processing industry in the clarification of juices by breakdown of the pectic substances therein (depectinization) as described in WO94/21786, WO95/34223 and FR2638064. German Patent Specification 3,635,427, published April 23, 1985 by Lion Corporation, is directed to phosphate-free detergents for cleaning clothes containing enzymes with pectinase activity.

However, the synergistic combination of a pectate lyase (EC 4.2.2.2) and a pectin lyase (EC 4.2.2.10), for superior cleaning performance in a detergent composition, has never been previously recognised.

Summary of the invention

The present invention relates to detergent compositions, including laundry, dishwashing, and hard surface cleaner compositions, comprising a pectate lyase and a pectin lyase, for superior cleaning performance, i.e. superior stain removal on plant-based stains/soils and body soils; dingy cleaning and whiteness maintenance.

Detailed description of the invention

The Pectate lyase enzyme

An essential element of the detergent composition of the present invention is a pectate lyase enzyme.

Pectate lyase is classified within the classification of enzymes provided by the Enzyme Nomenclature (1992) as EC 4.2.2.2. Said enzyme is known to split the

α -1,4,glucoside bond of galacturonic acid found in pectin substances, creating a double bond between C4 and C5 and is substantially free for other pectin degrading activities, i.e having less than 25%, preferably less than 15%, more preferably less than 5% by weight of the enzyme compound of other pectin degrading enzyme activities.

Pectate lyases have been cloned from different bacterial genera such as *Erwinia*, *Pseudomonas*, *Klebsiella*, *Streptomyces*, *Penicillium*, *Bacteroides*, *Thermomonospora*, *Fusarium*, *Aspergillus* and *Xanthomonas*. Also from *Bacillus subtilis* (Nasser et al. (1993) FEBS **335**:319-326) and *Bacillus* sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. **58**:947-949) cloning of a pectate lyase has been described. Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by *Bacillus pumilus* (Dave and Vaughn (1971) J. Bacteriol. **108**:166-174), *B. polymyxa* (Nagel and Vaughn (1961) Arch. Biochem. Biophys. **93**:344-352), *B. stearothermophilus* (Karbassi and Vaughn (1980) Can. J. Microbiol. **26**:377-384), *Bacillus* sp. (Hasegawa and Nagel (1966) J. Food Sci. **31**:838-845) and *Bacillus* sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. **24**:1164-1172) has been reported. WO 98/45393 discloses detergent compositions containing protopectinase with remarkable detergency against muddy soils.

Further suitable pectate lyases for use in the present invention are the protopectinases having an optimum reaction pH of 7.0 or higher when polygalacturonic acid is used as a substrate such as described in WO98/45393 and the pectic acid lyase having the amino acid sequence SEQ no 1 of EP 870 843 or having such amino acid sequence with one or more amino acid being deleted, added or substituted.

Preferred are the pectate lyase enzymes described in the international co-pending application PCT/DK98/00515, filed internationally on November 24, 1998 :

- A pectate lyase comprising a first amino acid sequence consisting of seven (7) amino acid residues having the following sequence: Asn Leu Asn Ser Arg Val Pro (NLNSRVP);
- A pectate lyase which is :
 - i) a polypeptide produced by *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus agaradhaerens*, DSM 8721, of at least 99%, or
 - ii) a polypeptide comprising an amino acid sequence as shown in positions 27-359 of SEQ ID NO:2 of PCT/DK98/00515, or
 - iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or
 - iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived polypeptide is at least 42% homologous with said polypeptide, or
 - v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;
- A pectate lyase which is :
 - i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus licheniformis*, ATCC 14580, of at least 99%, or
 - ii) a polypeptide comprising an amino acid sequence as shown in positions 28-341 of SEQ ID NO:4 of PCT/DK98/00515, or
 - iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or
 - iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 233, and

optionally also the arginine in position 238, is conserved and the derived polypeptide is at least 42% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;

- A pectate lyase which is :

i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:14 of PCT/DK98/00515 or by a *Bacillus* species having a 16S rDNA sequence homology to SEQ ID NO:14 of PCT/DK98/00515 higher than 97.3%; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 181-509 of SEQ ID NO:6 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) which is at least 50% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 390, and optionally also the arginine in position 395, is conserved and the derived polypeptide is at least 44% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

- A pectate lyase which is :

i) a polypeptide produced by the species *Bacillus halodurans*, or

ii) a polypeptide comprising an amino acid sequence as shown in positions 42-348 of SEQ ID NO:8 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived polypeptide is at least 40% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

- A pectate lyase which is

i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:13 or by a *Bacillus* species having a 16S rDNA sequence homology to SEQ ID NO:13 of PCT/DK98/00515 higher than 98.1%; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 25-335 of SEQ ID NO:10 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) or which is at least 45% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 227, and optionally also the arginine in position 232, is conserved and the derived polypeptide is at least 41% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Similarly preferred is the pectate lyase enzyme described in the international co-pending application PCT/DK98/00514, filed internationally on November 24, 1998 and which is :

i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or

ii) a polypeptide comprising an amino acid sequence as shown in positions 28-221 of SEQ ID NO:4 of PCT/DK98/00514, or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 60% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the lysines in positions 133 and 155 and the arginine in position 158 are conserved and the

derived polypeptide is at least 66% homologous with positions 60-158 of SEQ ID NO:4 of PCT/DK98/00514, or

- v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form

More preferred pectate lyases for the purpose of the present invention are those having optimum activity at pH's >7.0 and derived from *Streptomyces fradiae*, *Streptomyces nitrosporeus*, *Erwinia carotovora*, *Bacillus sphaeroides*, *Thermomonospora fusca*, *Pseudomonas solanacearum*, *Bacteroides thetaiotaomicron*, *Fusarium solani*, *Xanthomonas campestris*, *Bacillus agaradhaerens*, and/or *Bacillus licheniformis*.

Most preferred pectate lyase for the purpose of the present invention is the Pectate lyase from *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721.

The pectate lyase is incorporated into the compositions of the invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

The pectin lyase enzyme

An essential component of the detergent compositions of the invention is pectin lyase enzyme from the EC classification EC 4.2.2.10, substantially free of other pectic enzymes, which act on the pectic acids to bring about non-hydrolytic cleavage of alpha-1-4 glycosidic linkages to give oligosaccharides with terminal 4-deoxy-6- α -D-galacto-enuronosyl groups.

In a preferred embodiment, the detergent compositions of the present invention comprise an alkaline pectin lyase enzyme substantially free of other pectic enzymes. The term "alkaline" is intended to cover pectin lyase enzyme having an enzymatic activity of at least 10%, preferably 25%, more preferably 40% of its optimum activity, at a pH ranging from 7 to 11, preferably to cover pectin lyase enzyme having an optimum activity at a pH ranging from 7 to 11. The enzymatic activity can be measured according to the "Assay of trans-eliminase activities toward pectin and pectic acid" described by K. Horikoshi in *Agr. Biol. Chem.*, Vol 36(2), 286.

The pectin lyase of the present invention is substantially free of other pectic enzymes. By "substantially free of other pectic enzymes", it is meant pectin lyase enzyme-containing compositions which contain less than 25% of pectic enzymes which are not pectin lyase enzymes, preferably less than 15%, more preferably less than 5%.

The pectin lyase enzyme substantially free of other pectic enzymes is generally incorporated into the detergent compositions in accordance with the invention at a level of from 0.0001% to 2%, preferably from 0.0005% to 0.5%, more preferably from 0.001% to 0.1% pure enzyme by weight of the total composition.

Pectic substances may be found in plant tissues, and are common constituents of fruit juices such as orange, tomato and grape juices. Pectic substances contain polygalacturonic acids and/or their derivatives. They include pectins and pectic acids. Pectins are, in general, polymers made up of chains of galacturonic acids joined by alpha-1-4 glycosidic linkages. Typically, in natural pectins approximately two-thirds of the carboxylic acid groups are esterified with methanol. Partial hydrolysis of these methyl esters gives low methoxyl pectins, which tend to form gels with calcium ions. Complete methyl ester hydrolysis gives pectic acids.

Pectin lyase enzyme substantially free of other pectic enzymes herein include naturally derived pectin lyase enzymes and any variants obtained by, for example, genetic engineering techniques.

Pectin lyase enzyme substantially free of other pectic enzymes can be produced from *Bacillus* species, preferably from *B. firmus*, *B. circulans* and *B. subtilis* as described in J56131376. EP 353188 discloses a DNA sequence coding for a pectin lyase PLA, PLB, PPLC, PLE or PLF)ed or deleted, used to produce pectin lyases in pure form or for constructing hybrid vectors expressing foreign genes. A pectin lyase expression system used for over-production of pectin lyase in *Aspergillus* and/or for the construction of hybrid vectors expressing genes in filamentous fungi, is described in EP 278 355. Enzymes mixtures containing pectin lyase can be obtained from the submerged aerobic culture of certain *Aspergillus niger* strains as disclosed in HUT033216. J02035088 described also a pectin lyase gene useful for the production of said enzyme, deriving from genus *Erwinia* bacteria. Pectin lyase can also be of fungi origin - purified from pectin degrading enzyme mixture - such as *Aspergillus niger* and *Aspergillus japonicus*. Purified pectin lyase can be obtained by purification and/or fractionation via well known techniques in the art as described by K. Horikoshi in *Agr. Biol. Chem*, Vol 36(2), 288; by V. Shevchik et al. in *World Journal of Microbiology and Biotechnology*, Vol 8, (1992), 116 and by E. Harris et al. (1989), in "Protein purification methods, a practical approach" Ed IRL Press, Oxford, England.

Commercially available pectin lyase enzymes substantially free of other pectic enzymes include those sold under P7052 from *Aspergillus niger*, P2804 from *Aspergillus japonicus*, P5936 from *Aspergillus japonicus* and P2679 from *Aspergillus japonicus* by Sigma. Also available are the pectin lyase enzymes from *Aspergillus niger* sold from Worthington under the tradename LS04297, LS04298 and LS04296.

Preferred pectin lyase for the pupose of the present invention is the pectin lyase described in the co-pending international patent application PCT/DK98/00514, internationally filed on November 24, 1998 and which is

- i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 31-494 of SEQ ID NO:2 of PCT/DK98/00514, or
- iii) an analogue of the polypeptide defined in i) or ii) which is at least 60% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginins in positions 377 and 383 relative to SEQ ID NO:2 of PCT/DK98/00514 are conserved and that the derived polypeptide is at least 60% homologous with said polypeptide, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Preferably, the detergent compositions of the present invention will comprise these two enzymes at a level of from 0.0001% to 4%, more preferably from 0.0005% to 2%, most preferably from 0.001% to 1% pure enzyme by weight of the total composition. Preferably, the pectate lyase and pectin lyase will be comprised in the detergent compositions of the present invention at a weight ratio of pure enzyme of from 10:1 to 1:10, more preferably 5:1 to 1:5, most preferably 2:1 to 1:2.

The pectate lyase and/or pectin lyase encompassed in the detergent compositions of the present invention, in addition to the enzyme core comprising the catalytically domain, may also comprise a cellulose binding domain (CBD), the cellulose binding domain and enzyme core (the catalytically active domain) of the enzyme being operably linked. The cellulose binding domain (CBD) may exist as an integral part of the encoded enzyme, or a CBD from another origin may be

introduced into the enzyme thus creating an enzyme hybrid. In this context, the term "cellulose-binding domain" is intended to be understood as defined by Peter Tomme et al. "Cellulose-Binding Domains: Classification and Properties" in "Enzymatic Degradation of Insoluble Carbohydrates", John N. Saddler and Michael H. Penner (Eds.), ACS Symposium Series, No. 618, 1996. This definition classifies more than 120 cellulose-binding domains into 10 families (I-X), and demonstrates that CBDs are found in various enzymes such as cellulases, xylanases, mannanases, arabinofuranosidases, acetyl esterases and chitinases. CBDs have also been found in algae, e.g. the red alga *Porphyra purpurea* as a non-hydrolytic polysaccharide-binding protein, see Tomme et al., *op.cit.* However, most of the CBDs are from cellulases and xylanases, CBDs are found at the N and C termini of proteins or are internal. Enzyme hybrids are known in the art, see e.g. WO 90/00609 and WO 95/16782, and may be prepared by transforming into a host cell a DNA construct comprising at least a fragment of DNA encoding the cellulose-binding domain ligated, with or without a linker, to a DNA sequence encoding the pectate lyase and/or pectin lyase enzyme and growing the host cell to express the fused gene. Enzyme hybrids may be described by the following formula:



wherein CBD is the N-terminal or the C-terminal region of an amino acid sequence corresponding to at least the cellulose binding domain; MR is the middle region (the linker), and may be a bond, or a short linking group preferably of from about 2 to about 100 carbon atoms, more preferably of from 2 to 40 carbon atoms; or is preferably from about 2 to to about 100 amino acids, more preferably of from 2 to 40 amino acids; and X is an N-terminal or C-terminal region of the pectate lyase and/or pectin lyase of the invention.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic,

acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing metal binding sites to increase chelant stability.

Detergent components

The detergent compositions of the invention must contain at least one additional detergent component. The precise nature of these additional component, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

The detergent compositions of the present invention preferably further comprise a bleaching agent.

The detergent compositions according to the invention can be liquid, paste, gels, bars, tablets, spray, foam, powder or granular. Granular compositions can also

be in "compact" form and the liquid compositions can also be in a "concentrated" form. Tablet compositions can be in single phase or multiple phase form.

In a first embodiment, the present invention relates to a laundry and/or fabric care detergent compositions comprising a pectate lyase and a pectin lyase (Examples 1-15). In a second embodiment, the present invention relates to dishwashing or household detergent compositions (Examples 16-24).

The compositions of the invention may for example, be formulated as hand dishwashing compositions, hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics and compositions for use in general household hard surface cleaning operations. When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components. Such compositions containing a pectate lyase and pectin lyase can provide fabric cleaning, stain removal, and color appearance when formulated as laundry detergent compositions.

When formulated as compositions suitable for use in a machine dish wash method, the compositions of the invention preferably contain a low foaming nonionic surfactant, a builder system, and one or more components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

The compositions of the invention can also be used as detergent additive products in solid or liquid form. Such additive products are intended to supplement or boost the performance of conventional detergent compositions and can be added at any stage of the cleaning process.

If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 500 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition. In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition. The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides. A preferred filler salt is sodium sulphate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically the water content of the concentrated

liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

Suitable detergent compounds for use herein are selected from the group consisting of the below described compounds.

Bleaching agent

It has been surprisingly found that the detergent compositions of the present invention further comprising a bleaching agent, especially a bleach activator bleaching system, provide enhanced food stain removal and whiteness maintenance. Without wishing to be bound by theory, it is believed the smaller chromophoric particles resulting from the combined hydrolysis action of the pectate lyase and pectin lyase enzymes, are more easily attacked by the bleach activated system, especially at low temperature.

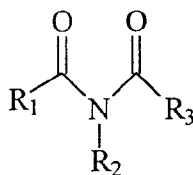
Preferred detergent ingredients that can be included in the detergent compositions of the present invention include bleaching agents such as hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetythylenediamine (TAED), nonanoyl-oxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5,-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7 and unsymmetrical acyclic imide bleach activator of the following formula as disclosed in the Procter & Gamble co-pending patent applications US serial No. 60/022,786 (filed July 30, 1996) and No. 60/028,122 (filed October 15, 1996) :



wherein R₁ is a C₇-C₁₃ linear or branched chain saturated or unsaturated alkyl group, R₂ is a C₁-C₈, linear or branched chain saturated or unsaturated alkyl group and R₃ is a C₁-C₄ linear or branched chain saturated or unsaturated alkyl group.

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

Surfactant system

The detergent compositions according to the present invention generally comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of detergent compositions in accord with the invention.

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Preferred surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

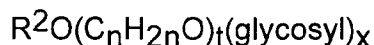
Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic

surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

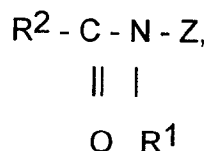
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with

the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.

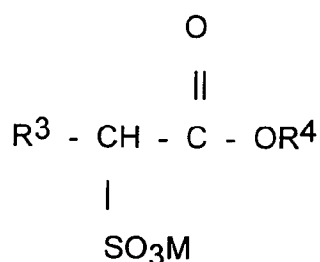


wherein R¹ is H, or R¹ is C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R¹ is methyl, R² is a straight C₁₁₋₁₅ alkyl or C₁₆₋₁₈ alkyl or alkenyl chain such as coconut alkyl or

mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C₈-C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃ according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



wherein R³ is a C₈-C₂₀ hydrocarbyl, preferably an alkyl, or combination thereof, R⁴ is a C₁-C₆ hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R³ is C₁₀-C₁₆ alkyl, and R⁴ is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R³ is C₁₀-C₁₆ alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or

ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethylammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g. below about 50°C) and C₁₆-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₈-C₂₂ primary or secondary alkanesulfonates, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k-CH_2COO-M^+$ wherein R is a C₈-C₂₂ alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

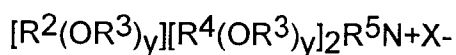
Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12} - $C_{18}E(1.0)M$), C_{12} - C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12} - $C_{18}E(2.25)M$), C_{12} - C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12} - $C_{18}E(3.0)M$), and C_{12} - C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12} - $C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

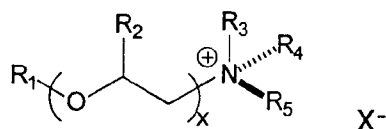
The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Cationic deterative surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



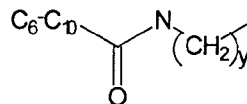
wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R⁴ groups, -CH₂CHOH-CHOHCOR⁶CHOHCH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



Formula I

whereby R₁ is a short chainlength alkyl (C₆-C₁₀) or alkylamidoalkyl of the formula (II) :



Formula II

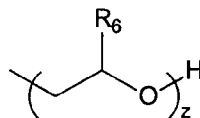
y is 2-4, preferably 3.

whereby R₂ is H or a C₁-C₃ alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R₃, R₄ and R₅ are either the same or different and can be either a short chain alkyl (C₁-C₃) or alkoxyated alkyl of the formula III,

whereby X⁻ is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

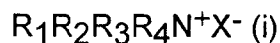
R₆ is C₁-C₄ and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby

R₁ is C₈, C₁₀ or mixtures thereof, x=0,

R₃, R₄ = CH₃ and R₅ = CH₂CH₂OH.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein R₁ is C₈-C₁₆ alkyl, each of R₂, R₃ and R₄ is independently C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl, benzyl, and -(C₂H₄)_xH where x has a value from 2 to 5, and X is an anion. Not more than one of R₂, R₃ or R₄ should be benzyl.

The preferred alkyl chain length for R_1 is C_{12} - C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;
 coconut methyl dihydroxyethyl ammonium chloride or bromide;
 decyl triethyl ammonium chloride;
 decyl dimethyl hydroxyethyl ammonium chloride or bromide;
 C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
 coconut dimethyl hydroxyethyl ammonium chloride or bromide;
 myristyl trimethyl ammonium methyl sulphate;
 lauryl dimethyl benzyl ammonium chloride or bromide;
 lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;
 choline esters (compounds of formula (i) wherein R_1 is $CH_2-CH_2-O-C-C_{12-14}$ alkyl and $R_2R_3R_4$ are methyl).



di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

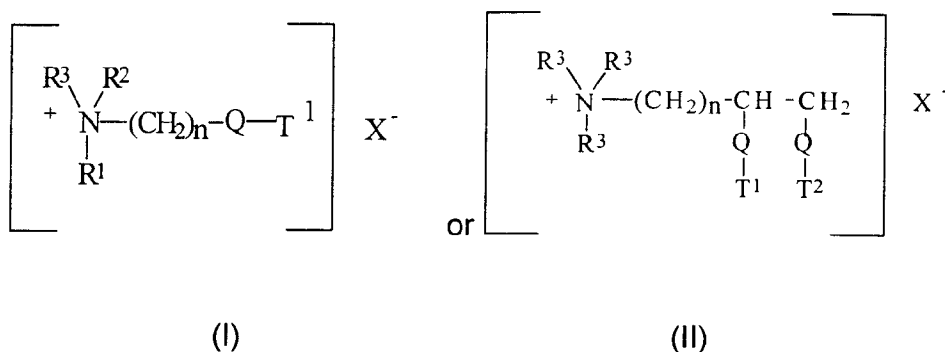
Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives or their corresponding amine precursor, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C₁₂₋₁₄ alkyl hydroxyethyl dimethylammonium chloride;
- 11) C₁₂₋₁₈ alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallow-oxy-ethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :



wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR⁴-C(O)-, -C(O)-NR⁴-;

R¹ is (CH₂)_n-Q-T² or T³;

R² is (CH₂)_m-Q-T⁴ or T⁵ or R³;

R³ is C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl or H;

R⁴ is H or C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl;

T¹, T², T³, T⁴, T⁵ are independently C₁₁-C₂₂ alkyl or alkenyl;

n and m are integers from 1 to 4; and

X⁻ is a softener-compatible anion. Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T¹, T², T³, T⁴, T⁵ must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched. Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T¹, T², T³, T⁴, T⁵ represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
- 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;

- 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
 - 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
 - 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
 - 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
 - 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride;
- and mixtures of any of the above materials.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

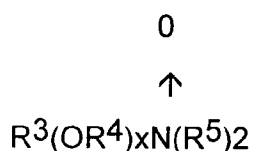
Zwitterionic surfactants are also suitable for use in detergent compositions. These surfactants can be broadly described as derivatives of secondary and

tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or

mixtures thereof; x is from 0 to about 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R⁵ groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides.

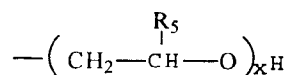
When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The detergent composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines.

Suitable primary amines for use herein include amines according to the formula R₁NH₂ wherein R₁ is a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain or R₄X(CH₂)_n, X is -O-, -C(O)NH- or -NH-, R₄ is a C₆-C₁₂ alkyl chain n is between 1 to 5, preferably 3. R₁ alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C₈-C₁₀ oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

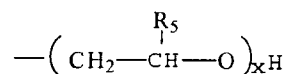
Suitable tertiary amines for use herein include tertiary amines having the formula R₁R₂R₃N wherein R₁ and R₂ are C₁-C₈ alkylchains or



R₃ is either a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain, or R₃ is R₄X(CH₂)_n, whereby X is -O-, -C(O)NH- or -NH-, R₄ is a C₄-C₁₂, n is between 1 to 5, preferably 2-3. R₅ is H or C₁-C₂ alkyl and x is between 1 to 6.

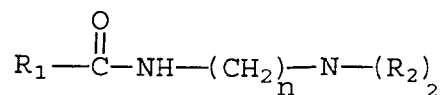
R₃ and R₄ may be linear or branched ; R₃ alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are R₁R₂R₃N where R₁ is a C₆-C₁₂ alkyl chain, R₂ and R₃ are C₁-C₃ alkyl or



where R₅ is H or CH₃ and x = 1-2.

Also preferred are the amidoamines of the formula:



wherein R₁ is C₆-C₁₂ alkyl; n is 2-4,
preferably n is 3; R₂ and R₃ is C₁-C₄

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C₈-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C₈-10 amidopropyldimethylamine and C₁₀ amidopropyldimethylamine.

The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

Conventional detergent enzymes

The detergent compositions can in addition to the pectate lyase and pectin lyase further comprise one or more enzymes which provide cleaning performance, fabric care and/or sanitisation benefits.

Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, other pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243.

Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is the protease called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue

positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04, 1997).

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to

0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial α -amylases products are Purafect Ox Am[®] from Genencor and Termamyl[®], Ban[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amyolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amyolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to

0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special attention must be paid to the cellulases as most of the cellulases have separate binding domains (CBD). Properties of such enzymes can be altered by modifications in these domains.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates,

stabilized liquids, etc. containing one enzyme) or as mixtures of two or more enzymes (e.g. cogramulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Colour care and fabric care benefits

Technologies which provide a type of colour care benefit can also be included. Examples of these technologies are metallo catalysts for colour maintenance. Such metallo catalysts are described in copending European Patent Application No. 92870181.2. Dye fixing agents, polyolefin dispersion for anti-wrinkles and improved water absorbancy, perfume and amino-functional polymer (PCT/US97/16546) for colour care treatment and perfume substantivity are

further examples of colour care / fabric care technologies and are described in the co-pending Patent Application No. 96870140.9, filed November 07, 1996.

Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

Builder system

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein

including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates,

1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid. Other preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid detergent compositions of the present invention are soaps and polycarboxylates.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most usually from 30% to 60% by weight.

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are

permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Suds suppressor

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable

carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components. A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^R.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Others

Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616. Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

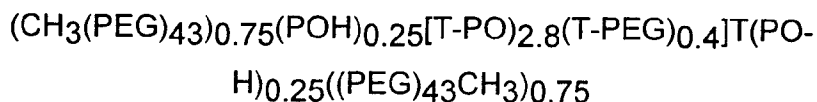
Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium

4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylami-no)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners disclosed in EP 753 567.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_n\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono

esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

It is well-known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the

range of about 2000 to about 50,000. Such alkoxyated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Dispersants

The detergent composition of the present invention can also contain dispersants : Suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000.

Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the detergent compositions of the present invention.

The compositions of the invention may contain a lime soap peptiser compound, which has preferably a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163,

(1990); and M.K. Nagarajan, W.F. Masler, *Cosmetics and Toiletries*, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm CaCO_3 (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include C_{16} - C_{18} dimethyl amine oxide, C_{12} - C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12} - C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3 (LSDP=4), and the C_{14} - C_{15} ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in *Cosmetics and Toiletries*, volume 104, pages 71-73, (1989).

Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof; and nonanoyloxy benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

Dye transfer inhibition

The detergent compositions of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

Polymeric dye transfer inhibiting agents

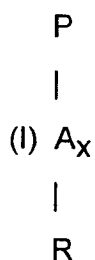
The detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof.

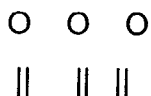
Addition of such polymers also enhances the performance of the enzymes according the invention.

a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :



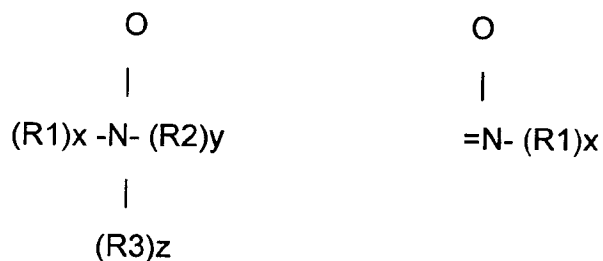
wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.



A is NC, CO, C, -O-, -S-, -N- ; x is 0 or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably,

the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a $\text{PKa} < 10$, preferably $\text{PKa} < 7$, more preferred $\text{PKa} < 6$.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinylloxazolidone :

The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

f) Cross-linked polymers :

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups in the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling. Such cross-linked polymers are described in the co-pending patent application 94870213.9

Method of washing

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting fabrics with a laundering solution in the usual manner and exemplified hereunder.

The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 12.

A preferred machine dishwashing method comprises treating soiled articles with an aqueous liquid having dissolved or dispensed therein an effective amount of the machine dishwashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a wash volume from 3-10 litres. According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the dishwashing composition, typically from 0.5-20g (per 25 dishes being treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the

detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

LAS	: Sodium linear C ₁₁₋₁₃ alkyl benzene sulphonate.
TAS	: Sodium tallow alkyl sulphate.
CxyAS	: Sodium C _{1x} - C _{1y} alkyl sulfate.
CxySAS	: Sodium C _{1x} - C _{1y} secondary (2,3) alkyl sulfate.
MBAS	: Mid-branched alkyl sulfate.
CxyEz	: C _{1x} - C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide.
CxyEzS	: C _{1x} - C _{1y} sodium alkyl sulfate condensed with an average of z moles of ethylene oxide.
CxEyOy	: Cy alcohol with an average of ethoxylation of y.
Nonionic	: Mixed ethoxylated/propoxylated fatty alcohol e.g. Plurafac LF404 being an alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.
QAS	: R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ -C ₁₄ .
SADS	: Sodium C ₁₄₋₂₂ alkyl disulfate of the formula 2-R.C ₄ H ₇ .-1,4-(SO ₄ -) ₂ where R = C ₁₀₋₁₈ .
MES	: x-sulpho methyl ester of C ₁₈ fatty acid.
APA	: C ₈₋₁₀ amido propyl dimethyl amine.
Soap	: Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut fatty acids.
Neodol xy-z	: C _{1x} -C _{1y} linear primary alcohol z ethoxylate.
CFAA	: C ₁₂ -C ₁₄ alkyl N-methyl glucamide.
TFAA	: C ₁₆ -C ₁₈ alkyl N-methyl glucamide.
TPKFA	: C ₁₂ -C ₁₄ topped whole cut fatty acids.
DEQA	: Di-(tallow-oxy-ethyl) dimethyl ammonium chloride.

DEQA (2)	: Di-(soft-tallowyloxyethyl) hydroxyethyl methyl ammonium methylsulfate.
DTDMAMS	: Ditallow dimethyl ammonium methylsulfate.
SDASA	: 1:2 ratio of stearyl dimethyl amine:triple-pressed stearic acid.
Silicate	: Amorphous Sodium Silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio = 1.6-3.2:1).
Metasilicate	: Sodium metasilicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio = 1.0).
Zeolite A	: Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers (Weight expressed on an anhydrous basis).
Na-SKS-6	: Crystalline layered silicate of formula $\delta\text{-Na}_2\text{Si}_2\text{O}_5$.
Citrate	: Tri-sodium citrate dihydrate.
Citric	: Anhydrous citric acid.
Borate	: Sodium borate
Carbonate	: Anhydrous sodium carbonate.
Bicarbonate	: Sodium hydrogen carbonate.
Sulphate	: Anhydrous sodium sulphate.
STPP	: Sodium tripolyphosphate.
TSP	: Tetrasodium pyrophosphate.
MA/AA	: Random copolymer of 4:1 acrylate/maleate, average molecular weight about 70,000-80,000.
MA/AA 1	: Random copolymer of 6:4 acrylate/maleate, average molecular weight about 10,000.
AA	: Sodium polyacrylate polymer of average molecular weight 4,500.

Polycarboxylate	: Copolymer comprising mixture of carboxylated monomers such as acrylate, maleate and methacrylate with a MW ranging between 2,000-80,000 such as Sokolan commercially available from BASF, being a copolymer of acrylic acid, MW4,500.
PB1	: Anhydrous sodium perborate monohydrate.
PB4	: Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$.
Percarbonate	: Anhydrous sodium percarbonate of nominal formula $2.74 \text{ Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$.
NaDCC	: Sodium dichloroisocyanurate.
TAED	: Tetraacetyl ethylene diamine.
NOBS	: Nonanoyloxybenzene sulfonate in the form of the sodium salt.
NACA-OBS	: (6-nonamidocaproyl) oxybenzene sulfonate.
DOBS	: Decanoyl oxybenzene sulfonate in the form of the sodium salt.
DTPA	: Diethylene triamine pentaacetic acid.
HEDP	: 1,1-hydroxyethane diphosphonic acid.
DETPMP	: Diethyltriamine penta (methylene) phosphonate, marketed by Monsanto under the Trade name Dequest 2060.
EDDS	: Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt
Chelant	: Chelant selected from EEDS, HEDP, DTPA, DETPMP and/or mixtures thereof.
MnTACN	: Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane.
Photoactivated Bleach	: Sulfonated zinc phthalocyanine encapsulated in dextrin soluble polymer.

Photoactivated Bleach 1	: Sulfonated alumino phtalocyanine encapsulated in dextrin soluble polymer.
PAAC	: Pentaamine acetate cobalt(III) salt.
Paraffin	: Paraffin oil sold under the tradename Winog 70 by Wintershall.
NaBz	: Sodium benzoate.
Pectate lyase	: Pectate lyase from <i>Bacillus agaradhaerens</i> , NCIMB 40482 or DSM 8721
Pectin lyase	: Pectin lyase produced by <i>Bacillus licheniformis</i> , ATCC 14580.
Protease	: Proteolytic enzyme sold under the tradename Savinase , Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.
Amylase	: Amylolytic enzyme sold under the tradename Purafact Ox Am ^R described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl [®] , Fungamyl [®] and Duramyl [®] , all available from Novo Nordisk A/S and those described in WO95/26397 (sold under the tradename Natalase By Novo Nordisk).
Lipase	: Lipolytic enzyme sold under the tradename Lipolase Lipolase Ultra by Novo Nordisk A/S and Lipomax by Gist-Brocades.
Cellulase	: Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.
CMC	: Sodium carboxymethyl cellulose.
PVNO	: Polyvinylpyridine-N-Oxide, with an average molecular weight of 50,000.

PVPVI	: Copolymer of vinylimidazole and vinylpyrrolidone, with an average molecular weight of 20,000.
Brightener 1	: Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
Brightener 2	: Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.
Silicone antifoam	: Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
Suds Suppressor	: 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form.
Opacifier	: Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621.
Thickener	: High molecular weight crosslinked polyacrylates such as Carbopol offered by B.F. Goodrich Chemical Company and Polygel.
SRP 1	: Anionically end capped poly esters.
SRP 2	: Diethoxylated poly (1,2 propylene terephthalate) short block polymer.
QEA	: $\text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3) - \text{N}^+ - \text{C}_6\text{H}_{12} - \text{N}^+ - (\text{CH}_3) \text{bis}((\text{C}_2\text{H}_5\text{O}) - (\text{C}_2\text{H}_4\text{O}))_n$, wherein $n = \text{from } 20 \text{ to } 30$.
SCS	: Sodium cumene sulphonate.
HMWPEO	: High molecular weight polyethylene oxide.
PEGX	: Polyethylene glycol, of a molecular weight of x .
PEO	: Polyethylene oxide, with an average molecular weight of 5,000.
TEPAE	: Tetraethylenepentaamine ethoxylate.
BTA	: Benzotriazole.
pH	: Measured as a 1% solution in distilled water at 20°C.

Example 1

The following high density and bleach-containing laundry detergent compositions were prepared according to the present invention:

	I	II	III
Blown Powder			
Zeolite A	12.0	-	15.0
Sulfate	-	5.0	-
LAS	3.0	-	3.0
C45AS	3.0	2.0	4.0
QAS	-	-	1.5
DETPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	1.0	2.0	2.0
Agglomerates			
QAS	1.0	-	-
LAS	-	11.0	7.0
TAS	2.0	2.0	1.0
Silicate	3.0	-	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Agglomerate			
NaSKS-6	15.0	12.0	5.0
LAS	8.0	7.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C25E3	2.0	-	2.0
Dry additives			

71

	I	II	III
QEA	1.0	0.5	0.5
Citric/Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED and/ or NACA-OBS	6.0	-	5.0
NOBS	-	2.0	-
Percarbonate/ PB1	14.0	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Citric acid	4.0	-	1.5
Pectate lyase	0.001	0.01	0.01
Pectin lyase	0.005	0.001	0.01
Protease	0.033	0.033	0.033
Lipase	0.008	0.008	0.008
Amylase	0.005	0.005	0.005
Cellulase	0.0014	0.0014	0.0014
Silicone antifoam	5.0	5.0	5.0
Sulfate	-	3.0	-
Density (g/litre)	850	850	850
Moisture and miscellaneous	Up to 100%		

Example 2

The following laundry compositions, which may be in the form of granules or tablet, were prepared according to the present invention.

I II III IV V

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	5.0	3.0	3.0	3.0
LAS	8.0	-	8.0	-	7.0
C25AE3S	0.5	2.0	1.0	-	-
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0
Zeolite A	20.0	18.0	11.0	-	10.0
SKS-6 (I) (dry add)	-	-	9.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0
Percarbonate	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.004	0.004	0.008	0.007	0.010
Lipase	0.006	0.003	0.005	0.003	0.008
Amylase	0.003	0.015	0.007	0.006	0.010
Cellulase	0.001	0.0015	0.001	0.0014	0.003
Pectate lyase	0.001	0.002	0.01	0.06	0.005
Pectin lyase	0.003	0.001	0.001	0.006	0.005

	I	II	III	IV	V
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1
Moisture and miscellaneous	Up to 100%				
Minors include Brightener / SRP1 / CMC / Photobleach / MgSO4 / PVPVI/ Suds suppressor /PEG.					

Example 3

The following high density laundry detergent compositions were prepared according to the present invention:

	I	II	III
Agglomerate			
QAS	2.0	-	2.0
MES	-	2.0	-
LAS	6.0	-	-
TAS	-	2.0	-
C45AS	6.0	4.0	2.0
MBAS16.5, 1.9	4.0	-	-
Zeolite A	15.0	6.0	-
Carbonate	4.0	8.0	4.0
MA/AA	4.0	2.0	-
CMC	0.5	0.5	-
DETPMP	0.4	0.4	-
Spray On			
C25E3	1.0	1.0	-
Perfume	0.5	0.5	0.5
Agglomerate			
SKS-6	7.0	15.0	20.0

	I	II	III
LAS	5.8	9.0	15.0
Zeolite	-	0.9	-
Water	0.08	0.1	-
Dry Adds			
EDDS/HEDP	0.5	0.3	0.5
NaSKS 6 (I)	5.0	6.0	4.0
Citrate	-	1.0	-
Citric	2.0	-	2.0
NACA-OBS	4.1	-	5.0
TAED	0.8	2.0	-
Percarbonate	20.0	20.0	15.0
SRP 1	0.3	0.3	-
Pectate lyase	0.005	0.02	0.03
Pectin lyase	0.05	0.002	0.02
Protease	0.046	0.046	0.033
Lipase	0.008	0.008	0.006
Cellulase	0.0014	0.0014	0.001
Amylase	0.01	0.01	-
QEA	1.0	-	1.0
Silicone antifoam	1.0	0.5	0.5
Brightener 1	0.2	0.2	-
Brightener 2	0.2	-	0.2
Density (g/litre)	850	850	800
Moisture and miscellaneous		Up to 100%	

Example 4

The following laundry compositions, which may be in the form of granules or tablet, were prepared in accordance with the invention:

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	5.0	3.0	3.0	3.0
LAS	8.0	-	8.0	-	7.0
C25AE3S	0.5	2.0	1.0	-	-
LAS/NaSKS-6	5.0	17.0	9.0	20.0	15.0
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0
Zeolite A	20.0	10.0	10.0	-	10.0
SKS-6	-	-	2.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0
PC	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.004	0.004	0.008	0.007	0.010
Lipase	0.006	0.003	0.005	0.003	0.008

	I	II	III	IV	V
Amylase	0.003	0.015	0.007	0.006	0.010
Cellulase	0.001	0.0015	0.001	0.0014	0.003
Pectate lyase	0.002	0.01	0.01	0.015	0.03
Pectin lyase	0.0002	0.003	0.01	0.054	.008
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1
Moisture and miscellaneous	Up to 100%				
Minors include Brightener / SRP1 / CMC / Photobleach / MgSO4 / PVPVI/ Suds suppressor /PEG.					

Example 5

The following high density laundry detergent compositions were prepared according to the present invention:

	I	II	III	IV
Agglomerate				
QAS	2.0	-	2.0	-
MES	-	2.0	-	-
LAS	6.0	-	-	-
TAS	-	2.0	-	-
C45AS	6.0	4.0	2.0	-
MBAS16.5, 1.9	4.0	-	-	-
Zeolite A	15.0	6.0	-	-
Carbonate	4.0	8.0	4.0	8.0
MA/AA	4.0	2.0	-	2.0
CMC	0.5	0.5	-	0.5
DETPMP	0.4	0.4	-	0.5
Spray On				

	I	II	III	IV
C25E3	1.0	1.0	-	-
Perfume	0.5	0.5	0.5	0.5
Agglomerate				
SKS-6	7.0	15.0	20.0	10.0
LAS	5.8	9.0	15.0	10.0
Zeolite	-	0.9	-	-
C45 AS	-	3.0	-	-
Water	0.08	0.1	-	0.2
Dry Adds				
EDDS/HEDP	0.5	0.3	0.5	0.8
NaSKS 6)	5.0	6.0	4.0	11.0
Citrate	-	1.0	-	-
Citric	2.0	-	2.0	4.0
NAC OBS	4.1	-	5.0	4.0
TAED	0.8	2.0	-	2.0
Percarbonate	20.0	20.0	15.0	17.0
SRP 1	0.3	0.3	-	0.3
Pectate lyase	0.01	0.02	0.001	0.002
Pectin lyase	0.005	0.005	0.01	0.02
Protease	0.046	0.046	0.033	0.016
Lipase	0.008	0.008	0.006	-
Cellulase	0.0014	0.0014	0.001	0.001
Amylase	0.004	0.004	-	0.002
QEA	1.0	-	1.0	1.0
Silicone antifoam	1.0	0.5	0.5	1.5
Brightener 1	0.2	0.2	-	6.2
Brightener 2	0.2	-	0.2	-
Density (g/litre)	850	850	800	775
Moisture and miscellaneous		Up to 100%		

Example 6

The following granular detergent were prepared in accordance with the present invention:

	I	II	III	IV
Base granule				
STPP	-	22.0	-	15.0
Zeolite A	30.0	-	24.0	5.0
Sulfate	5.5	5.0	7.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AE11S	-	1.0	-	1.0
MES	0.5	4.0	6.0	-
SADS	2.5	-	-	1.0
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	8.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray on				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-

	I	II	III	IV
Perfume	0.2	0.3	0.3	-
Dry additives				
Carbonate	5.0	10.0	13.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	0.033	0.033	0.033	0.0016
Lipase	0.008	-	-	0.008
Amylase	0.0016	-	-	0.0016
Cellulase	0.0002	0.0005	0.0005	0.0002
Pectate lyase	0.001	0.02	0.03	0.015
Pectin lyase	0.0004	0.002	0.034	0.004
DTPA	0.5	0.3	0.5	1.0
PB1	5	3.0	10	4.0
NOBS/ TAED	0.5	0.3	0.5	0.6
Sulfate	4.0	5.0	-	5.0
SRP1	-	0.4	-	-
Sud supressor	-	0.5	-	-
speckle	0.9	-	2.7	1.2
Moisture and miscellaneous	Up to 100%			

Example 7

The following laundry detergent compositions were prepared in accordance with the present invention:

	I	II	III	IV	V	VI	VII
LAS	12.0	16.0	23.0	19	18.0	20.0	16.0
C45AS		4.5	-		-	-	4.0
C45 E0.5S			-	-	-	-	-
C45 E3S	-	-	2.0	-	1.0	1.0	1.0

	I	II	III	IV	V	VI	VII
C45E6.5S	2.0	2.0	-	1.3	-	-	0.6
C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt			-	-	1.0	0.5	2.0
Tallow fatty acid			-	-	-	-	1.0
Tallow alcohol ethoxylate (50)	-	-	-	-	-	-	-
STPP	23.0	25.0	24.0	22.0	20.0	15.0	20.0
Carbonate	15.0	12.0	15.0	10.0	13.0	11.0	10.0
Sodium Polyacrylate (45%)	0.5	0.5	0.5	0.5	-	-	-
MA/AA	-	-	1.0	1.0	1.0	2.0	0.5
Silicate (1:6 ratio	3.0	6.0	9.0	8.0	9.0	6.0	8.0
Sulfate	25.0	18.0	20.0	18.0	20.0	22.0	13.0
PB1	5.0	5.0	10.0	8.0	3.0	1.0	2.0
PEG MW ~4000 (50%)	1.5	1.5	1.0	1.0	-	-	0.5
CMC	1.0	1.0	1.0	-	0.5	0.5	0.5
Citric	-	-	-	-	-	-	-
NOBS/ DOBS	0.5	1.0	0.5	0.5	1.0	0.7	0.3
TAED	1.5	1.0	2.5	3.0	0.3	0.2	0.5
SRP1	1.5	1.5	1.0	1.0	-	1.0	-
SRP2	-	-	-	-	1.0	-	1.0
Moisture	7.5	7.5	6.0	7.0	5.0	3.0	5.0
Mg sulphate	-	-	-	-	1.0	0.5	1.5
Chelant	-	-	-	-	0.8	0.6	1.0
Protease	0.004	0.004	0.008	0.007	0.010	0.007	0.010
Lipase	0.006	0.003	0.005	0.003	0.008	0.003	0.008
Amylase	0.003	0.015	0.007	0.006	0.010	0.006	0.010
Cellulase	.001	.0015	.001	.0014	0.003	.0014	0.003

	I	II	III	IV	V	VI	VII
Pectate lyase	0.001	0.02	0.01	0.001	0.002	0.005	0.03
Pectin lyase	.0008	0.004	0.006	0.001	0.01	0.001	0.001
speckle	2.5	4.1	4.2	4.4	5.6	5.0	5.2
Minors	1.0	1.0	1.0	1.0	0.5	1.5	1.0

Example 8

The following laundry detergent compositions were prepared in accordance with the present invention:

	I	II	III	IV
LAS	13.3	13.7	10.4	8.0
C ₄₅ AS	3.9	4.0	4.5	-
C ₄₅ E0.5S	2.0	2.0	-	-
C ₄₅ E3S	-	-	-	-
C ₄₅ E6.5S	0.5	0.5	0.5	5.0
C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt	1.0	-	-	0.5
Tallow fatty acid	0.5	-	-	-
Tallow alcohol ethoxylate (50)	-	-	1.0	0.3
STPP	-	41.0	-	20.0
Zeolite A	26.3	-	21.3	1.0
Carbonate	23.9	12.4	25.2	17.0
Sodium Polyacrylate (45%)	3.4	0.0	2.7	-
MA/AA	-	-	1.0	1.5
Silicate (1:6 ratio)	2.4	6.4	2.1	6.0
Sulfate	10.5	10.9	8.2	15.0
PB1	1.0	1.0	1.0	2.0
PEG MW ~4000 (50%)	1.7	0.4	1.0	-
CMC	1.0	-	-	0.3
Citric	-	-	3.0	-
NOBS/ DOBS	0.2	0.5	0.5	0.1
TAED	0.6	0.5	0.4	0.3
SRP 1	1.5	-	-	-
SRP2	-	1.5	1.0	1.0

	I	II	III	IV
Moisture	7.5	3.1	6.1	7.3
Mn sulphate	-	-	-	1.0
Chelant	-	-	-	0.5
speckles	0.5	1.0	3.0	0.5
Pectate lyase	0.001	0.01	0.006	0.002
Pectin lyase	0.008	0.008	0.06	0.01
Protease	0.004	0.004	0.008	0.007
Lipase	0.006	0.003	0.005	0.003
Amylase	0.003	0.015	0.007	0.006
Minors	1.0	1.0	1.0	1.0

Example 9

The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme):

	I	II	III	IV	V
LAS	11.5	9.0	-	4.0	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	16.0	-
C23E9	-	3.0	2.0	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.0	-	3.0
TPKFA	2.0	-	2.0	0.5	2.0
Citric (50%)	6.5	1.0	2.5	4.0	2.5
Ca formate	0.1	0.06	0.1	-	-
Na formate	0.5	0.06	0.1	0.05	0.05
SCS	4.0	1.0	3.0	1.2	-

	I	II	III	IV	V
Borate	0.6	-	3.0	2.0	3.0
Na hydroxide	6.0	2.0	3.5	4.0	3.0
Ethanol	2.0	1.0	4.0	4.0	3.0
1,2 Propanediol	3.0	2.0	8.0	8.0	5.0
Monoethanolamine	3.0	1.5	1.0	2.5	1.0
TEPAE	2.0	-	1.0	1.0	1.0
Pectate lyase	0.1	0.002	0.01	0.01	0.005
Pectin lyase	0.01	0.001	0.04	0.001	0.0005
Protease	0.03	0.01	0.03	0.02	0.02
Lipase	-	-	0.002	-	-
Amylase	-	-	-	0.002	-
Cellulase	-	-	0.0002	0.0005	0.0001
SRP 1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Miscellaneous and water					

Example 10

The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme):

	I	II	III	IV	I	II	III	IV
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0

	I	II	III	IV	I	II	III	IV
APA	-	1.4	-	-	3.0	1.0	2.0	-
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0
Citric	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl / tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Rapeseed fatty acid	4.0	2.0	1.0	-	1.0	-	3.5	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0
Triethanolamine	-	-	8.0	-	-	-	0.4	0.3
TEPAE	0.5	-	0.5	0.2	2.0	1.2	1.0	-
DETPMP	1.0	1.0	0.5	1.0				
Pectate lyase	0.01	.001	.001	0.02	0.02	.002	.002	0.02
Pectin lyase	0.04	.005	.001	0.02	.015	.001	.005	.005
Protease	0.02	0.02	0.01	.008	-	-	.003	.003
Lipase	-	.002	-	.002	.004	0.01	0.01	0.01
Amylase	.004	.004	0.01	.008	-	-	.004	.003
Cellulase	-	-	-	.002	-	-	0.2	0.1
SRP 2	0.3	-	0.3	0.1	1.0	1.5	2.5	2.5
Boric acid	0.1	0.2	1.0	2.0	4.0	4.0	-	-
Ca chloride	-	0.02	-	0.01	0.1	0.2	0.3	-
Brightener 1	-	0.4	-	-	0.4	-	-	-
Suds suppressor	0.1	0.3	-	0.1	0.8	0.7	-	-
Opacifier	0.5	0.4	-	0.3	8.0	7.5	8.0	8.2
NaOH up to pH	8.0	8.0	7.6	7.7				
Miscellaneous and water								

Example 11

The following liquid detergent compositions were prepared according to the present invention (Levels are given in parts by weight, enzyme are expressed in pure enzyme):

	I	II
LAS	28.0	19.0
C45AS	14.0	6.0
C13E8	3.0	3.0
Oleic acid	3.0	2.5
Citric	5.0	5.0
Na hydroxide	0.4	4.0
Ca Formate	0.2	0.1
Na Formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	6.0	5.5
Xylene sulfonic acid	-	2.0
TEPAE	1.5	0.8
Protease	0.05	0.02
Pectate lyase	0.02	0.01
Pectin lyase	0.08	0.004
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume	0.5	0.3
Water and Minors		

Example 12

The following granular fabric detergent compositions which provide "softening through the wash" capability were prepared according to the present invention :

	I	II
C45AS	-	10.0
LAS	7.6	-
C68AS	1.3	-
C45E7	4.0	-
C25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
PB1	15.0	-
Percarbonate	-	15.0
TAED	5.0	5.0
Smectite clay	10.0	10.0
HMWPEO	-	0.1
Pectate lyase	0.001	0.01
Pectin lyase	0.001	0.01
Protease	0.02	0.01
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.001	-
Silicate	3.0	5.0
Carbonate	10.0	10.0

	I	II
Suds suppressor	1.0	4.0
CMC	0.2	0.1
Miscellaneous and minors	Up to 100%	

Example 13

The following rinse added fabric softener composition was prepared according to the present invention :

DEQA (2)	20.0
Pectate lyase	0.001
Pectin lyase	0.001
Cellulase	0.001
HCL	0.03
Antifoam agent	0.01
Blue dye	25ppm
CaCl ₂	0.20
Perfume	0.90
Miscellaneous and water	Up to 100%

Example 14

The following fabric softener and dryer added fabric conditioner compositions were prepared according to the present invention :

	I	II	III	IV	V
DEQA	2.6	19.0	-	-	-
DEQA(2)	-	-	-	-	52.0
DTMAMS	-	-	-	26.0	-

	I	II	III	IV	V
SDASA	-	-	70.0	42.0	40.2
Stearic acid of IV=0	0.3	-	-	-	-
Neodol 45-13	-	-	13.0	-	-
HCL	0.02	0.02	-	-	-
Ethanol	-	-	1.0	-	-
Pectate lyase	0.001	0.002	0.01	0.01	0.005
Pectin lyase	0.002	0.02	0.001	0.001	0.005
Perfume	0.3	1.0	0.75	1.0	1.5
Glycoperse S-20	-	-	-	-	15.4
Glycerol monostearate	-	-	-	26.0	-
Digeranyl Succinate	-	-	0.38	-	-
Silicone antifoam	0.01	0.01	-	-	-
Electrolyte	-	0.1	-	-	-
Clay	-	-	-	3.0	-
Dye	10ppm	25ppm	0.01	-	-
Water and minors	100%	100%	-	-	-

Example 15

The following laundry bar detergent compositions were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	VI	V	III	VI	V
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Na Laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0

	I	II	III	VI	V	III	VI	V
Ca Carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DETPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP 1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Pectate lyase	0.01	0.001	0.005	0.02	0.02	0.001	0.001	0.01
Pectin lyase	0.009	.002	0.005	0.005	0.004	0.003	0.008	0.01
Amylase	-	-	0.01	-	-	-	0.002	-
Protease	-	0.004	-	0.003	0.003	-	-	0.003
Lipase	-	0.002	-	0.002	-	-	-	-
Cellulase	-	.0003	-	-	.0003	.0002	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
Brightener	0.15	0.1	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

Example 16

The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	-	51.0	51.0	-	-	44.3
Citrate	17.0	-	-	50.0	40.2	-
Carbonate	17.5	14.0	20.0	-	8.0	33.6
Bicarbonate	-	-	-	26.0	-	-
Silicate	15.0	15.0	8.0	-	25.0	3.6
Metasilicate	2.5	4.5	4.5	-	-	-
PB1	10.0	8.0	8.0	-	-	-
PB4	-	-	-	10.0	-	-
Percarbonate	-	-	-	-	11.8	4.8
Nonionic	2.0	1.5	1.5	3.0	1.9	5.9
TAED	2.0	-	-	4.0	-	1.4
HEDP	1.0	-	-	-	-	-
DETPMP	0.6	-	-	-	-	-
MnTACN	-	-	-	-	0.01	-
PAAC	-	0.01	0.01	-	-	-
Paraffin	0.5	0.4	0.4	0.6	-	-
Pectate lyase	0.04	0.01	0.003	0.005	0.005	0.005
Pectin lyase	0.01	0.01	0.0005	0.008	0.033	0.004
Protease	0.072	0.053	0.053	0.026	0.059	0.01
Amylase	0.012	0.012	0.012	0.021	0.021	0.006
Lipase	-	0.001	-	0.005	-	-
BTA	0.3	0.2	0.2	0.3	0.3	0.3
Polycarboxylate	6.0	-	-	-	4.0	0.9
Perfume	0.2	0.1	0.1	0.2	0.2	0.2
pH	11.0	11.0	11.3	9.6	10.8	10.9
Miscellaneous, sulfate and water	Up to 100%					

Example 17

The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	30.0	33.5	27.9	29.6	33.8	22.0
Carbonate	30.5	30.5	30.5	23.0	34.5	45.0
Silicate	7.0	7.5	12.6	13.3	3.2	6.2
Metasilicate	-	4.5	-	-	-	-
Percarbonate	-	-	-	-	4.0	-
PB1	4.4	4.5	4.3	-	-	-
NADCC	-	-	-	2.0	-	0.9
Nonionic	1.0	0.7	1.0	1.9	0.7	0.5
TAED	1.0	-	-	-	0.9	-
PAAC	-	0.004	-	-	-	-
Paraffin	0.25	0.25	-	-	-	-
Pectate lyase	0.04	0.005	0.001	0.02	0.02	0.01
Pectin lyase	0.005	0.001	0.007	0.08	0.033	0.004
Protease	0.036	0.021	0.03	-	0.006	-
Amylase	0.03	0.005	0.004	-	0.005	-
Lipase	0.005	-	0.001	-	-	-
BTA	0.15	0.15	-	-	0.2	-
Perfume	0.2	0.2	0.05	0.1	0.2	-
pH	10.8	11.3	11.0	10.7	11.5	10.9
Miscellaneous, sulfate and water	Up to 100%					

Example 18

The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm² using a standard 12 head rotary press:

	I	II	III	IV	V	VI	VII	VIII
STPP	-	48.8	54.7	38.2	-	52.4	56.1	36.0
Citrate	20.0	-	-	-	35.9	-	-	-
Carbonate	20.0	5.0	14.0	15.4	8.0	23.0	20.0	28.0
Silicate	15.0	14.8	15.0	12.6	23.4	2.9	4.3	4.2
Pectate lyase	0.001	0.001	0.001	.0004	0.002	0.02	0.01	0.005
Pectin lyase	0.007	0.003	0.004	.0008	0.001	0.05	0.01	0.001
Protease	0.042	0.072	0.042	0.031	0.052	0.023	0.023	0.029
Amylase	0.012	0.012	0.012	0.007	0.015	0.003	0.017	0.002
Lipase	0.005	-	-	-	-	-	-	-
PB1	14.3	7.8	11.7	12.2	-	-	6.7	8.5
PB4	-	-	-	-	22.8	-	3.4	-
Percarbonate	-	-	-	-	-	10.4	-	-
Nonionic	1.5	2.0	2.0	2.2	1.0	4.2	4.0	6.5
PAAC	-	-	0.02	0.009	-	-	-	-
MnTACN	-	-	-	-	0.007	-	-	-
TAED	2.7	2.4	-	-	-	2.1	0.7	1.6
HEDP	1.0	-	-	0.9	-	0.4	0.2	-
DETPMP	0.7	-	-	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.5	-	-	0.5	-
BTA	0.2	0.3	0.3	0.3	0.3	0.3	0.3	-
Polycarboxylate	4.0	-	-	-	4.9	0.6	0.8	-
PEG	-	-	-	-	-	2.0	-	2.0
Glycerol	-	-	-	-	-	0.4	-	0.5
Perfume	-	-	-	0.05	0.2	0.2	0.2	0.2
Weight of tablet	20g	25g	20g	30g	18g	20g	25g	24g

Example 19

The following liquid dishwashing detergent compositions of density 1.40Kg/L were prepared according to the present invention :

	I	II	III	IV
STPP	17.5	17.2	23.2	23.1
Carbonate	-	2.4	-	-
Silicate	6.1	24.9	30.7	22.4
NaOCl	1.1	1.1	1.1	1.2
Thickener	1.0	1.1	1.1	1.0
Nonionic	-	0.1	0.06	0.1
NaBz	0.7	-	-	-
Pectate lyase	0.005	0.001	0.002	0.01
Pectin lyase	0.009	0.0044	0.006	0.053
NaOH	1.9	-	-	-
KOH	3.6	3.0	-	-
Perfume	0.05	-	-	-
pH	11.7	10.9	10.8	11.0
Water	up to 100%			

Example 20

The following liquid rinse aid compositions were prepared according to the present invention :

	I	II	III	IV
Pecate lyase	0.001	0.001	0.002	0.05
Pectin lyase	0.001	0.002	0.002	0.01

	I	II	III	IV
Nonionic	10.0	13.6	62.3	60.0
Propylene glycol	-	-	5.0	5.5
Citric	3.5	4.6	-	-
SCS	10.0	7.7	-	-
pH of the liquid	3.0	2.5	7.2	7.2
Miscellaneous, solvent and water	Up to 100%			

Example 21

The following manual liquid dishwashing compositions were prepared according to the present invention :

	I	II	III	IV	V	VI	VII
C12-14E06-2S	25.0	28.0	26.0	30.0	20.0	26.0	26.0
C12-14 alkyl dimethyl amine oxide	2.0	6.0	6.0	7.8	5.0	6.0	6.0
C12-14 alkyl dimethyl betaine	2.0	-	-	-	-	-	-
C12-14 glucose amide	3.0	1.0	-	-	-	-	-
C11EO9	-	1.0	-	4.0	2.0	-	-
C9-11EO8	5.0	-	3.0	-	-	3.0	3.0
DTPA	-	0.1	-	-	-	-	-
SCS	-	1.0	3.5	3.0	2.5	3.5	3.5
Xylene sulfonate	-	3.0	-	-	-	-	-
Mg hydroxide	1.0	-	-	-	-	-	-
Mg chloride	0.4	2.6	-	-	-	-	-
1,3 bis (methylamino) cyclohexane	-	-	0.7	1.0	0.3	2.5	0.7

	I	II	III	IV	V	VI	VII
N,N-dimethylamino) ethyl methacrylate homopolymer	-	-	0.2	0.5	0.2	0.2	0.2
Citric	-	-	3.0	-	-	-	-
Maleic acid	-	-	-	2.5	-	-	-
Ethanol	8.0	5.0	7.0	7.0	4.0	7.0	7.0
Protease	-	-	-	-	-	-	0.02
Amylase	-	-	-	-	-	0.005	-
Pectate lyase	0.005	0.001	0.02	0.002	0.005	0.01	0.001
Pectin lyase	0.001	0.008	0.055	0.008	0.004	0.01	0.005
Perfume	0.2	0.5	0.5	0.4	0.3	0.5	0.5
Water and minors	Up to 100%						

Example 22

The following liquid hard surface cleaning compositions were prepared according to the present invention :

	I	II	III	IV	V
Pectate lyase	0.005	0.1	0.02	0.02	0.005
Pectin lyase	0.003	0.4	0.067	0.08	0.001
Amylase	0.01	0.002	0.005	-	-
Protease	0.05	0.01	0.02	-	-
Hydrogen peroxide	-	-	-	6.0	6.8
Acetyl triethyl citrate	-	-	-	2.5	-
DTPA	-	-	-	0.2	-
Butyl hydroxy toluene	-	-	-	0.05	-
EDTA*	0.05	0.05	0.05	-	-
Citric / Citrate	2.9	2.9	2.9	1.0	-

	I	II	III	IV	V
LAS	0.5	0.5	0.5	-	-
C12 AS	0.5	0.5	0.5	-	-
C10AS	-	-	-	-	1.7
C12(E)S	0.5	0.5	0.5	-	-
C12,13 E6.5 nonionic	7.0	7.0	7.0	-	-
Neodol 23-6.5	-	-	-	12.0	-
Neodol 23-3	-	-	-	-	1.5
Neodol 91-10	-	-	-	-	1.6
C25AE1.8S	-	-	-	6.0	
Na paraffin sulphonate	-	-	-	6.0	
Perfume	1.0	1.0	1.0	0.5	0.2
Propanediol	-	-	-	1.5	
Ethoxylated tetraethylene pentamine	-	-	-	1.0	-
2, Butyl octanol	-	-	-	-	0.5
Hexyl carbitol**	1.0	1.0	1.0	-	-
SCS	1.3	1.3	1.3	-	-
pH adjusted to	7-12	7-12	7-12	4	-
Miscellaneous and water	Up to 100%				
*Na4 ethylenediamine diacetic acid					
**Diethylene glycol monohexyl ether					

Example 23

The following spray composition for cleaning of hard surfaces and removing household mildew was prepared according to the present invention :

Pectate lyase	0.01
Pectin lyase	0.001

Amylase	0.01
Protease	0.01
Na octyl sulfate	2.0
Na dodecyl sulfate	4.0
Na hydroxide	0.8
Silicate	0.04
Butyl carbitol*	4.0
Perfume	0.35
Water/minors	up to 100%
*Diethylene glycol monobutyl ether	

Example 24

The following disinfecting compositions were prepared according to the present invention.

	I	II	III
	Wipe	Spray	Liquid
H ₂ O ₂	1.0	1.5	1.0
Na tetraborate 10.H ₂ O	-	1.0	-
C10 Amine Oxide	-	0.9	0.9
C12-14 alkyl dimethyl amine oxide	0.4	-	-
C7-10 AS	-	-	6.0
C9-11EO10	-	0.05	-
C8-18 Fatty acid	-	0.1	0.2
Ethanol	9.0	1.0	2.5
Benzyl alcohol	-	0.8	-
Propylene or diethylene glycol butyl ether	1.0	1.5	-
Poly(propylene glycol) monobutyl ether	0.2	-	-
HEDP	-	0.1	-

100

	I	II	III
Butylated hydroxytoluene	0.01	0.06	0.03
Salicyclic acid	0.03	-	0.07
Pectate lyase	0.001	0.001	0.005
Pectin lyase	0.001	0.008	0.05
Perfume	0.1	0.3	0.3
Citric	0.7	-	1.5
Dye	-	-	2.0
NaOH	-	0.1	-
Miscellaneous and water	Up to 100%		

CLAIMS

1. A detergent composition comprising a detergent ingredient, a pectate lyase enzyme (EC 4.2.2.2) and a pectin lyase (EC 4.2.2.10) enzyme.
2. A detergent composition according to claim 1 wherein said pectate lyase is present at a level of from 0.0001% to 2%, preferably from 0.0005% to 0.5%, more preferably from 0.001% to 0.1% pure enzyme by weight of total composition.
3. A detergent composition according to claims 1-2 wherein said pectin lyase is present at a level of from 0.0001% to 2%, preferably from 0.0005% to 0.5%, more preferably from 0.001% to 0.1% pure enzyme by weight of total composition.
4. A detergent composition according to claims 1-3 wherein said pectin lyase and pectate lyase are comprised at a total level of 0.0001% to 4%, preferably from 0.0005% to 2%, more preferably from 0.001% to 1%.
5. A detergent composition according to claims 1-4 wherein said pectate lyase and pectin lyase are comprised at a weight ratio of pure enzyme of from 10:1 to 1:10, more preferably 5:1 to 1:5, most preferably 2:1 to 1:2.
6. A detergent composition according to any of the preceding claims wherein said detergent ingredient is a bleaching agent, preferably a bleach activator bleaching system.
7. Method of cleaning a fabric, dishware and/or hard surface with a detergent composition according to any of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/00790

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/386 //C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 98 06808 A (THE PROCTER & GAMBLE CO.) 19 February 1998 (1998-02-19) page 5, paragraph 4 -page 6, paragraph 4 page 15, paragraph 2 -page 18, paragraph 2 claims 1-3,7,8,12-14; examples 15,17 -----	1-4,6,7 5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

20 September 1999

Date of mailing of the international search report

04/10/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Serbetsoglou, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/00790

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9806808 A	19-02-1998	AU 6769996 A EP 0925346 A	06-03-1998 30-06-1999
<hr/>			